

## Electronic Supplementary Information for

### **Sb@C coaxial nanotubes as superior long-life and high-rate anode for sodium ion batteries**

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### **Experimental Section**

*Synthesis of Sb<sub>2</sub>S<sub>3</sub> nanorods:* The Sb<sub>2</sub>S<sub>3</sub> nanorods were synthesized through a simple hydrothermal method. In a typical synthesis, 4 mmol of SbCl<sub>3</sub>, 8 mmol of L-cysteine, and 8 mmol of Na<sub>2</sub>S 9H<sub>2</sub>O were orderly dissolved in 80 mL of distilled water (DIW) under stirring for 3 h to form a homogeneous suspension. Afterwards, the above solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and then kept at 180 °C for 12 h. After cooling down to room temperature naturally, the obtained dark-brown product was separated by centrifugation, washed with DIW and ethanol for several time before drying at 60 °C overnight under vacuum.

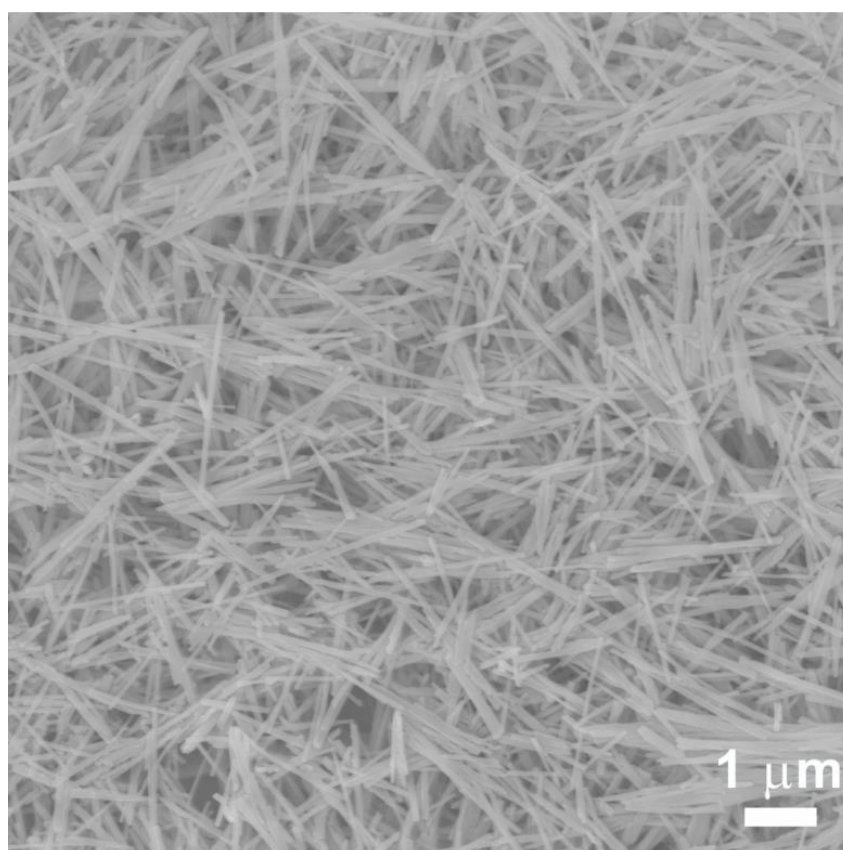
*Synthesis of Sb<sub>2</sub>S<sub>3</sub>@PDA core-shelled nanorods:* 30 mg of Sb<sub>2</sub>S<sub>3</sub> nanorods and 40 mg of dopamine hydrochloride were dispersed into 100 mL of Tris-buffer solution (10 mM) with

sonication for 10 minutes and then magnetic-stirring for 3 h. The resultant product was collected via centrifugation and washed with DIW and ethanol for three times, respectively, and dried at 60 °C overnight under vacuum.

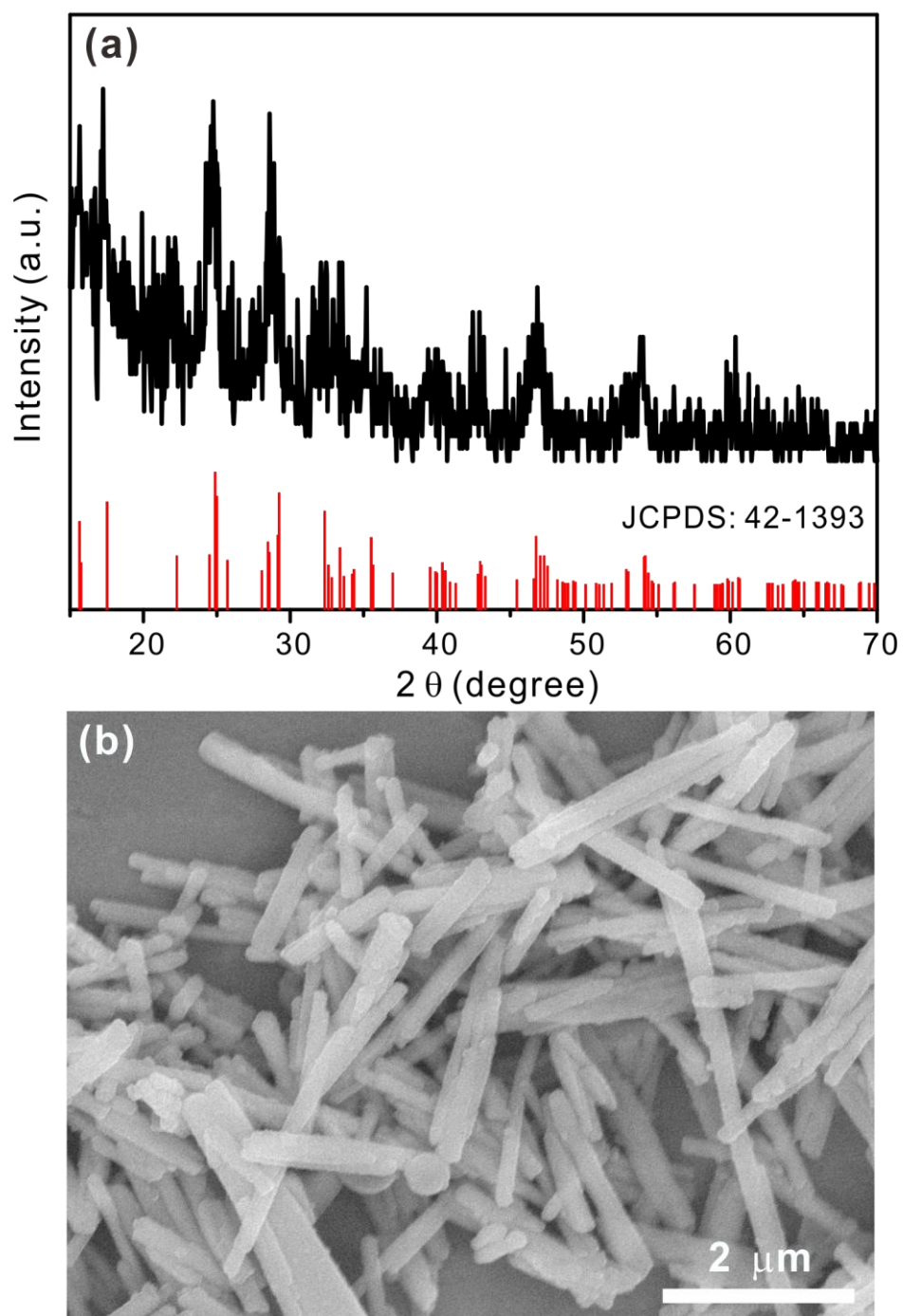
*Synthesis of Sb@C coaxial nanotubes:* Sb<sub>2</sub>S<sub>3</sub> nanorods were annealed at 500 °C for 1 h in Ar with a heating rate of 3 °C min<sup>-1</sup>. The as-prepared Sb<sub>2</sub>S<sub>3</sub>@PDA core-shelled nanorods were annealed at 500 °C in Ar with a heating rate of 3 °C min<sup>-1</sup> for 2, 5, 20, and 40 min, respectively. After different annealing time, Sb<sub>2</sub>S<sub>3</sub>@PDA core-shelled nanorods are transformed into Sb@C double-walled nanotubes.

*Materials characterization:* Field-emission scanning electron microscope (FESEM; JEOL JSM07600F) and transmission electron microscope (TEM; JEOL JEM-2100F) were used to characterize the microscopic features of the samples. A Rigaku D/MAX RINT-2000 X-Ray Diffractometer with Cu K $\alpha$  radiation at a voltage of 40 kV and a current of 40 mA was used to collect the XRD patterns of the products. Thermogravimetric analysis (TGA) was performed with a temperature ramp of 10 °C min<sup>-1</sup> under air flow.

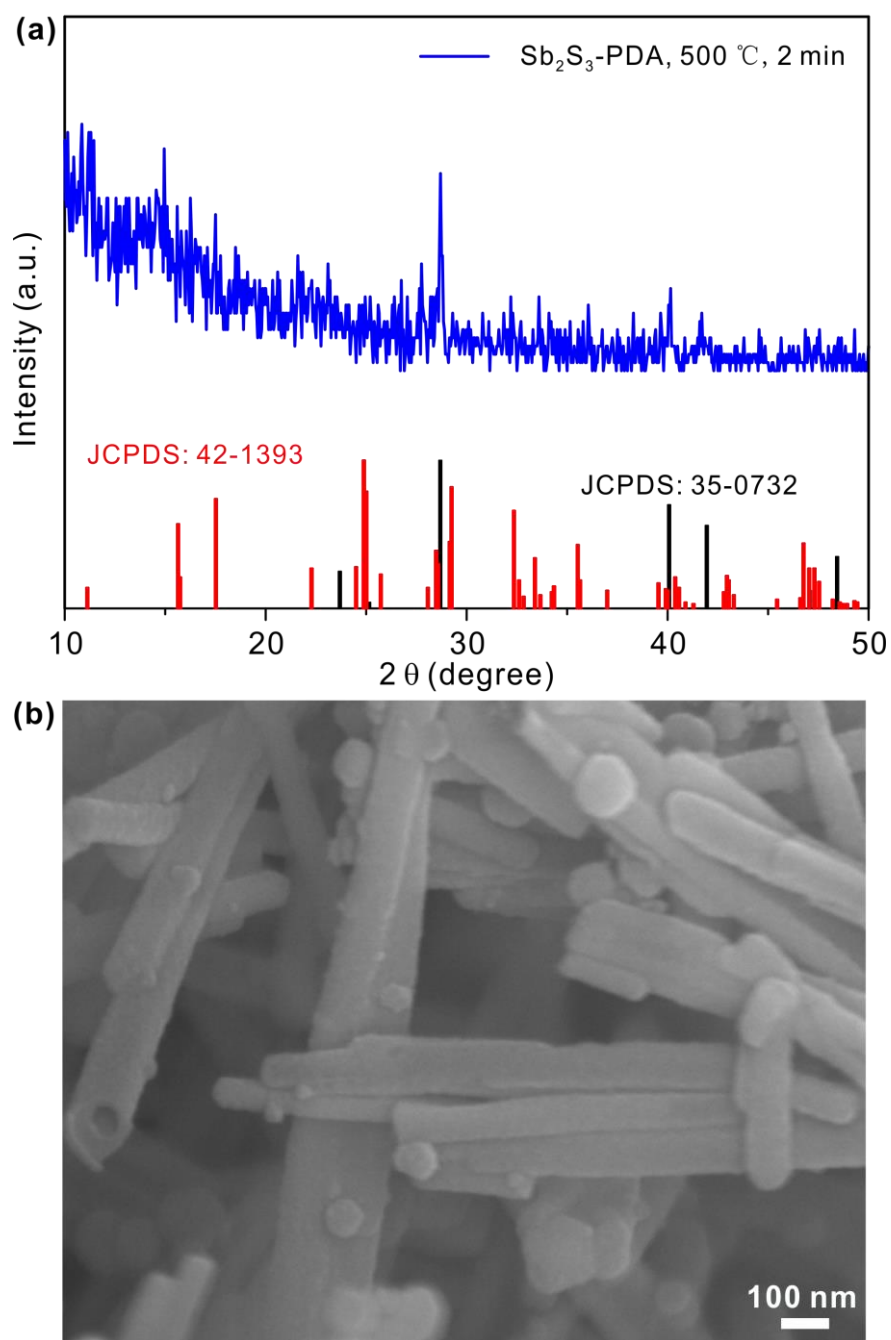
*Electrochemical measurements:* The battery tests were carried out in a half-cell configuration. The working electrode consists of active materials, conductivity agent (Carbon black, CB), and binder (Carboxymethylcellulose sodium, CMC-Na) with a weight ratio of 70:20:10. The mass loading of active materials was about 0.9 mg. The electrolyte was a solution of 1.0 M NaClO<sub>4</sub> in propylene carbonate with 5% fluoroethylene carbonate (FEC) additive. Sodium metal was used as both the counter electrode and reference electrode. The coin-type half cells were assembled in argon-filled glovebox and then tested in TOSCAT 3000 battery tester (TOSCAT 3000, Toyo Systems, Tokyo, Japan) with a voltage range between 0.01 and 2.0 V. Cyclic Voltammetry (CV) curves were tested using AUTOLAB potentiostat/galvanostat apparatus (AUT85698) with a scan rate of 0.1 mV s<sup>-1</sup>.



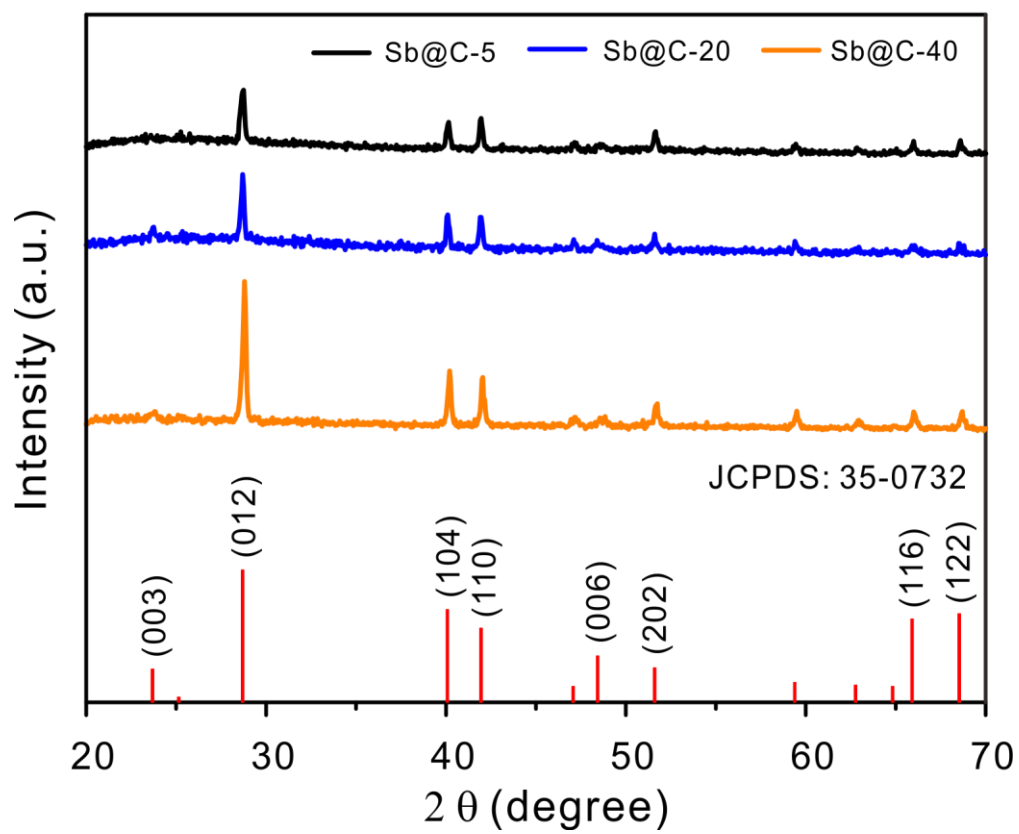
**Fig. S1** FESEM image of  $\text{Sb}_2\text{S}_3$  nanorods.



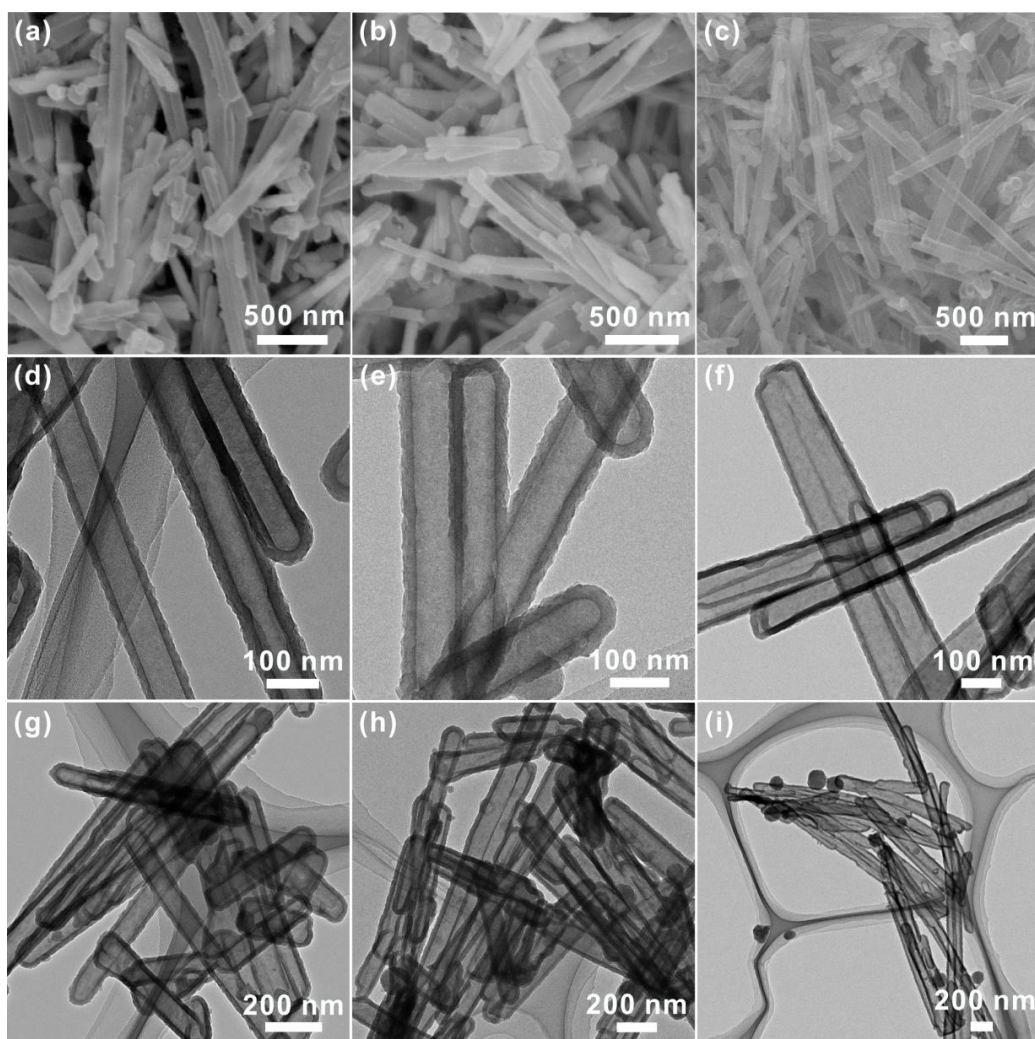
**Fig. S2** XRD pattern and FESEM image of  $\text{Sb}_2\text{S}_3$ @PDA core-shell nanorods.



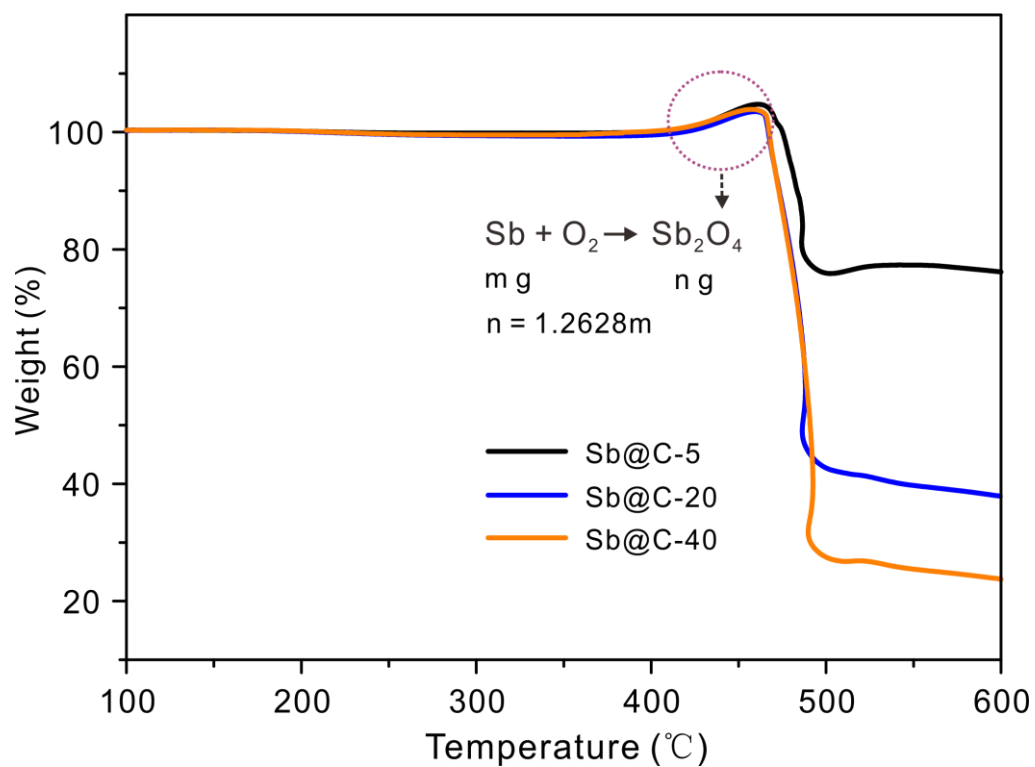
**Fig. S3** XRD pattern (a) and FESEM image (b) of  $\text{Sb}_2\text{S}_3\text{@PDA-2}$ .



**Fig. S4** XRD patterns of Sb@C-5, Sb@C-20, and Sb@C-40.

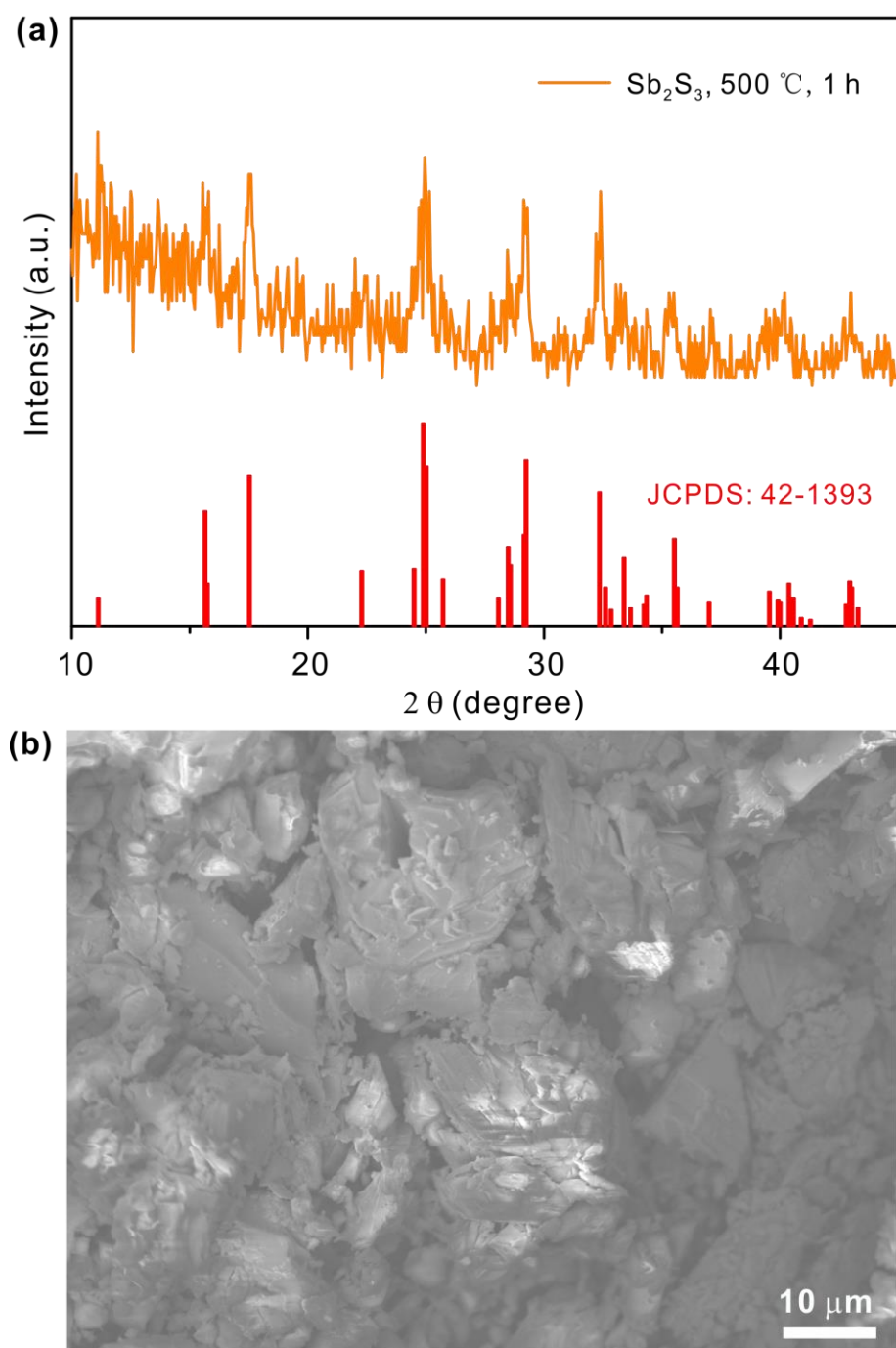


**Fig. S5** FESEM (a, b, c) and TEM (c, e, f, g, h, i) images of Sb@C-5 (a, d, g), Sb@C-20 (b, e, h), and Sb@C-40 (c, f, i).

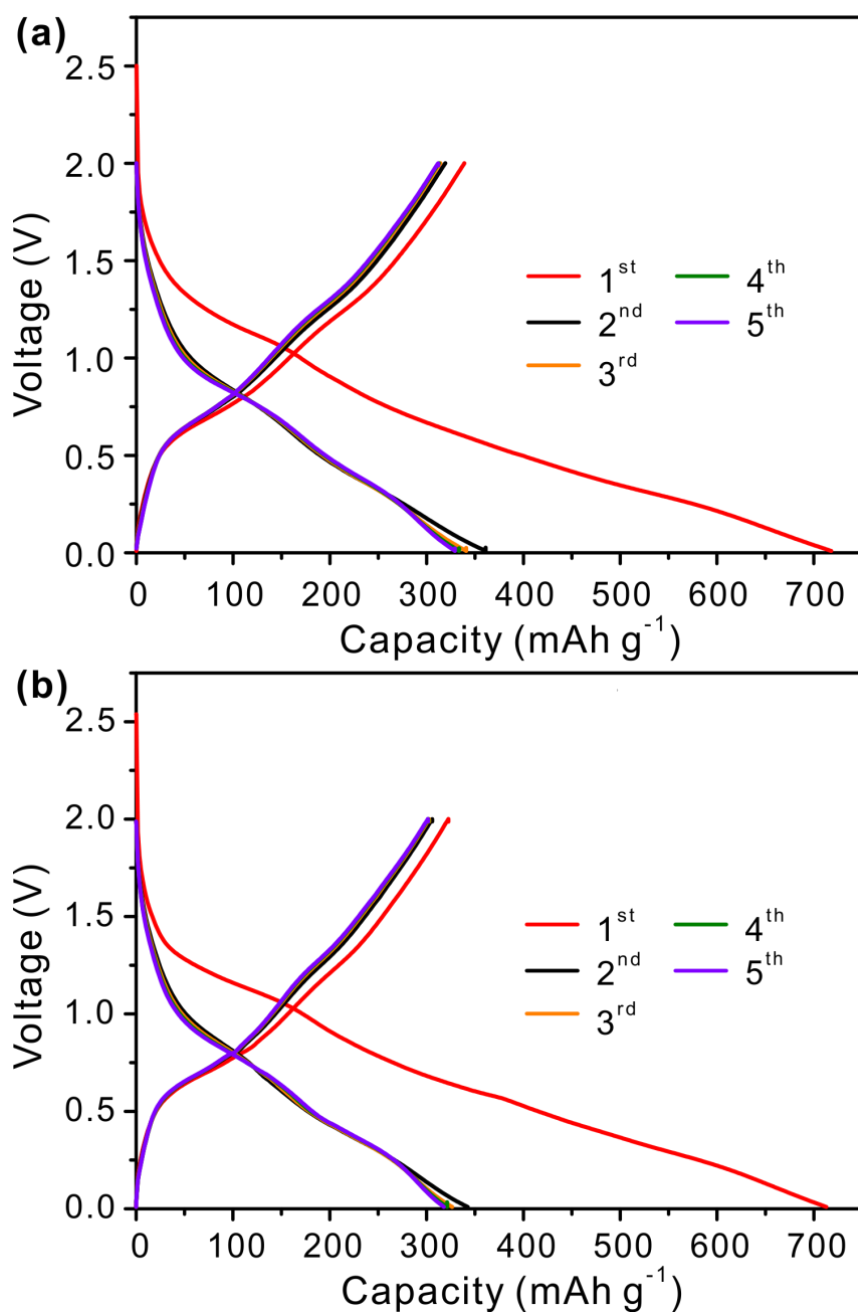


**Fig. S6** TGA analysis of Sb@C coaxial nanotubes at a temperature ramp of  $10\text{ }^{\circ}\text{C min}^{-1}$  in air.

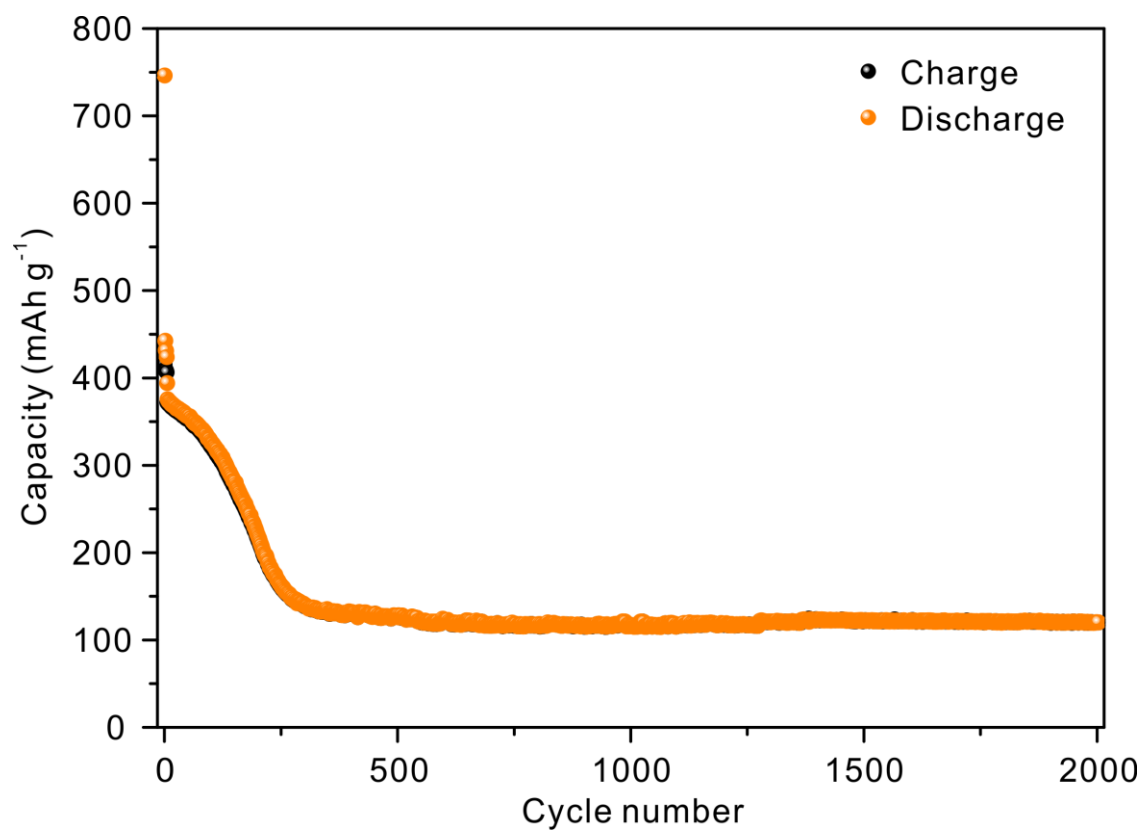




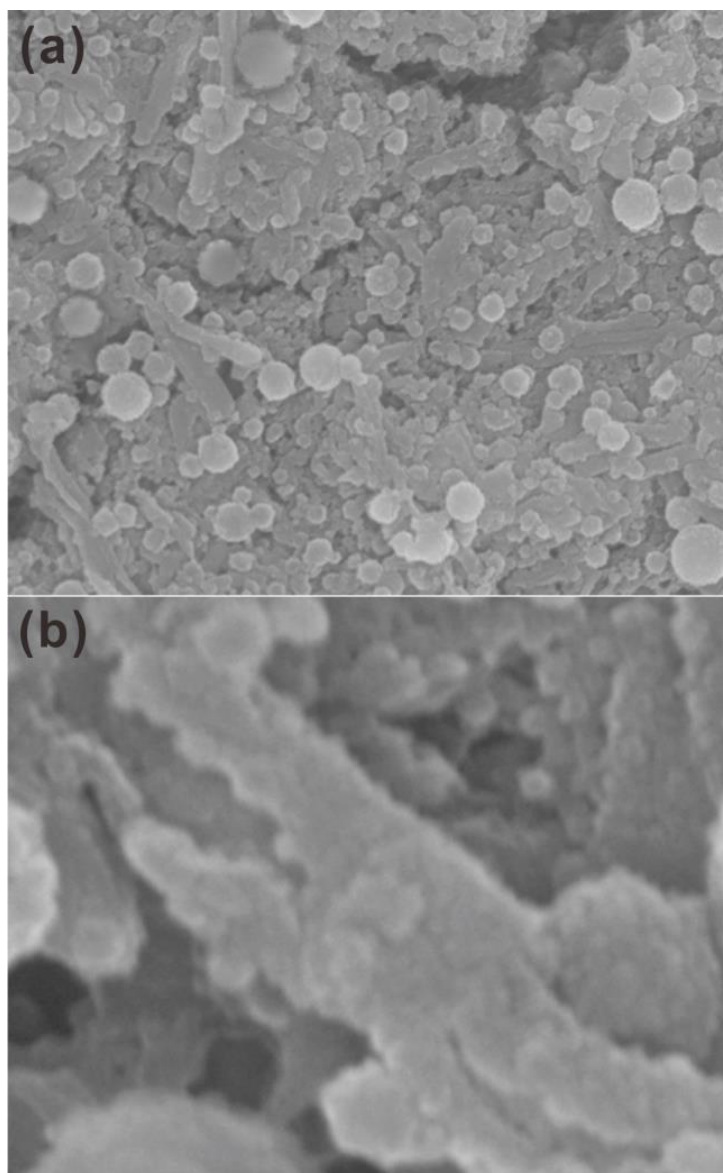
**Fig. S7** XRD pattern and FESEM image of  $\text{Sb}_2\text{S}_3$  nanorods after annealing at 500 °C for 1 h in Ar.



**Fig. S8** Charge-discharge voltage profiles of Sb@C-20 (a) and Sb@C-40 (b) for the first five cycles at a current density of  $100 \text{ mA g}^{-1}$ .



**Fig. S9** Cycling performance of Sb<sub>2</sub>S<sub>3</sub>@PDA-2 at a current density of 1.0 A g<sup>-1</sup>.



**Fig. S10** FESEM images of Sb@C-5 after 2000 cycles at a current density of  $1.0 \text{ A g}^{-1}$ .

**Table S1.** Comparison of some representative Sb-based anode materials for SIBs.

Sb-based anodes	Cycling performance	Rate capability	Ref.
Sb nanoparticles decorated N-rich carbon nanosheets	305 mAh g <sup>-1</sup> after 60 cycles at 50 mA g <sup>-1</sup>	142 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>	[1]
Sb/C nanofibers	350 mAh g <sup>-1</sup> after 300 cycles at 100 mA g <sup>-1</sup>	88 mAh g <sup>-1</sup> at 6 A g <sup>-1</sup>	[2]
Sb-C nanofibers	385 mAh g <sup>-1</sup> after 500 cycles at 100 mA g <sup>-1</sup>	337 mAh g <sup>-1</sup> at 3 A g <sup>-1</sup>	[3]
Sb hollow nanosphere	622.2 mAh g <sup>-1</sup> after 50 cycles at 50 mA g <sup>-1</sup>	315 mAh g <sup>-1</sup> at 1.6 A g <sup>-1</sup>	[4]
Sb porous hollow microspheres	574 mAh g <sup>-1</sup> after 100 cycles at 660 mA g <sup>-1</sup>	313 mAh g <sup>-1</sup> at 3.2 A g <sup>-1</sup>	[5]
Spherical nano-Sb@C composite	385 mAh g <sup>-1</sup> after 500 cycles at 100 mA g <sup>-1</sup>	270 mAh g <sup>-1</sup> at 4 A g <sup>-1</sup>	[6]
Sb/Multilayer Graphene hybrid	405 mAh g <sup>-1</sup> after 200 cycles at 100 mA g <sup>-1</sup>	210 mAh g <sup>-1</sup> at 5 A g <sup>-1</sup>	[7]
Sb/MWCNT nanocomposite	380 mAh g <sup>-1</sup> after 120 cycles at 200 mA g <sup>-1</sup>	225 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>	[8]
Sb @C coaxial nanotubes	407 mAh g <sup>-1</sup> after 240 cycles at 100 mA g <sup>-1</sup>	460 mAh g <sup>-1</sup> at 100 mA g <sup>-1</sup>	Present work
		350 mAh g <sup>-1</sup> at 10 A g <sup>-1</sup>	
	230 mAh g <sup>-1</sup> after 2000 cycles at 1 A g <sup>-1</sup>	310 mAh g <sup>-1</sup> at 20 A g <sup>-1</sup>	

## References

- [1] X. Zhou, Y. Zhong, M. Yang, M. Hu, J. Wei, Z. Zhou, *Chem. Commun.* **2014**, 50, 12888-12891.
- [2] Y. Zhu, X. Han, Y. Xu, Y. Liu, S. Zheng, K. Xu, L. Hu, C. Wang, *ACS Nano* **2013**, 7, 6378-6386.
- [3] L. Wu, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang, Y. Cao, *Energy Environ. Sci.* **2014**, 7, 323-328.
- [4] H. Hou, M. Jing, Y. Yang, Y. Zhu, L. Fang, W. Song, C. Pan, X. Yang, X. Ji, *ACS Appl. Mater. Interfaces* **2014**, 6, 16189-16196.
- [5] H. Hou, M. Jing, Y. Yang, Y. Zhang, Y. Zhu, W. Song, X. Yang, X. Ji, *J. Mater. Chem. A* **2015**, 3, 2971-2977.

- [6] N. Zhang, Y. Liu, Y. Lu, X. Han, F. Cheng, J. Chen, *Nano Research* **2015**, 8, 3384-3393.
- [7] L. Hu, X. Zhu, Y. Du, Y. Li, X. Zhou, J. Bao, *Chem. Mater.* **2015**, 27, 8138-8145.
- [8] X. Zhou, Z. Dai, J. Bao, Y.-G. Guo, *J. Mater. Chem. A* **2013**, 1, 13727.